# RELATION BETWEEN STRUCTURE AND PROPERTIES IN LINEAR POLYESTERS

BY

JOHN HARPSTER JOHNSON

B.S., University of Toledo, 1942

## AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

# RELATION BETWEEN STRUCTURE AND PROPERTIES IN LINEAR POLYESTERS

BY

JOHN HARPSTER JOHNSON

B.S., University of Toledo, 1942

## AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

## ACKNOWLEDGMENT

The author would like to express his sincere appreciation to Professor C. S. Marvel for suggesting this study and for his guidance and advice during the course of the investigation.

The author is indebted to the Allied Chemical and Dye Corporation for the fellowship under which the majority of this work was completed.

R. UNIV. BIBLIOTHEEK LEIDEN

# RELATION BETWEEN STRUCTURE AND PROPERTIES IN LINEAR POLYESTERS

## Introduction

Many ideas have been expressed concerning the effect of molecular structure on the properties of polymeric substances. However, very few closely related polymers with minor structural changes have been compared under controlled conditions of preparation and molecular size. The result is that there is actually little experimental evidence in the literature to show the contribution of such changes (i.e. the presence of a triple bond) to the properties of the polymer.

The present work was undertaken to prepare pairs of polymers of the same size which would have in one case a $-CH_2CH_2-$ unit and in the other a $-C\equiv C-$ unit with the remainder of the structure identical. To accomplish this purpose the two glycols $HOCH_2CH_2CH_2CH_2OH$ and $HOCH_2C\equiv CCH_2OH$ have been converted to polyesters of sebacic acid and to polyurethans by reaction with hexamethylene diisocyanate. Certain copolymers of the two glycols with the diisocyanate have also been prepared in order to make use of Flory's ideas for the determination of the contribution of each structure to the heat and entropy of fusion.[1] These values would be an indication of the bonding forces and stiffness of the polymer chain and are thus related to its physical properties.

## Discussion Of Results

A study has been made of various catalysts for the bulk condensation polymerization of dimethyl sebacate with 1,4 butanediol and with 1,4 butynediol. Lead oxide (litharge) and pyrophoric lead were found to be the best catalysts for the preparation of the saturated polyesters. Experimental observations were made which led to the postulation of a new mechanism of catalysis. This mechanism was based upon a

reaction between the pyrophoric metal and the glycol to form the metal salt. This metal salt acted as an intermediate in a series of chain reactions which resulted in the splitting-out of methyl alcohol and subsequent polymer formation. In accordance with this mechanism, new polymerization conditions were developed which gave faster polymerization rates and whiter polymers. Litharge and pyrophoric lead may be used to catalyze the preparation of butyne sebacates. However, they also catalyze the cross-linking reaction of the resultant polymers. The use of sebacic acid instead of the dimethyl ester, without other catalyst, appears to be the best method for the preparation of the butynediol ester. Other catalysts which were evaluated for the condensation reactions were Raney nickel, pyrophoric iron, *p*-toluenesulfonic acid, barium oxide, and sodium methoxide.

Polyurethans have been prepared by allowing hexamethylene diisocyanate to react with the 1,4 butanediol and with 1,4 butynediol in a solution of chlorinated benzenes. This solution polymerization is a modification of a similar method developed by the Germans in their work on polyurethans during the war. The reaction proceeds very readily at the reflux temperature of the solvent (about 132°), and no catalysts are needed. The polymers precipitate from solution upon cooling.

The nature and properties of these polymers have been investigated by various means. The saturated polymers in both series were white crystalline powders. They could be prepared with a sufficiently high molecular weight so that they could easily be drawn into fibers from the molten state. These fibers were subject to orientation upon cold-drawing with the resultant increase in transparency and fiber strength. The unsaturated polymers were susceptible to oxidative and thermal attack with the formation of insoluble cross-linked chains and dark coloration. They could be prepared colorless by using antioxidants, but it was difficult to prepare them of a sufficiently high molecular weight so that fibers could be drawn. The unsaturated polymers melt about 30° lower than the

corresponding saturated ones. The polycarboxylic esters are soluble in chloroform, dimethyl formamide, and *m*-cresol. The polyurethans are soluble in *m*-cresol and to a limited extent in dimethyl formamide. An indication of the molecular weights of the polymers was obtained from solution viscosities using chloroform solutions of the polyesters and *m*-cresol solutions of the polyurethans. Infrared and powder X-ray diffraction patterns were determined as a means of characterizing the polymers.

Two experimental tests were made to determine how these polymers would behave at very low temperatures. At normal temperatures they exhibit a degree of amorphous nature and elasticity. Second order transition temperature measurements were made to determine the temperature at which they lost this elasticity and became brittle upon cooling. These results indicated that polymers with acetylenic unsaturation became brittle at temperatures 30-40° higher than the corresponding saturated polymers. The saturated polymers had second order transition temperatures of about $-60$ to $-70°$. In the polyurethan series another test was run to determine the heat of fusion (bonding forces) and entropy of fusion (stiffness) for the polymers. They were determined from the observed lowering of melting points caused by the introduction of a known percentage of a foreign glycol according to the method developed by Flory. The butyne polyurethan had considerably lower values for both heat and entropy of fusion when compared to its saturated analogue. This indicates a straighter and a stiffer polymer which would be expected to become brittle at relatively high temperatures. Therefore, the presence of the acetylenic bond is detrimental to polymers which are to be used at low temperatures.

## BIBLIOGRAPHY

1. Flory, J. Chem. Phys., 15, 685 (1947).

## VITA

The author was born in Perrysburg, Ohio, on May 22, 1921. He attended public schools there through the eighth grade. He attended Rossford High School, Rossford, Ohio where he graduated in June, 1939. In September of that year he entered the University of Toledo, Toledo, Ohio, from which he received the degree of Bachelor of Science in Chemistry in September of 1942. From that date until June of 1946 he was employed as a chemist by United States Rubber Company, Charleston, West Virginia. After resigning from this position, he entered the graduate school of the University of Illinois in June, 1946. Since that date, he has held a half-time teaching assistantship in the Department of Chemistry for the years 1946-7 and 1947-8 and the Allied Chemical and Dye Corporation Fellowship from September, 1948 to June, 1949.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549807_0053